

6.4.3 MEASUREMENT

The pH of a water sample can change significantly within hours or even minutes after sample collection as a result of degassing (such as loss of carbon dioxide, hydrogen sulfide, and ammonia); mineral precipitation (such as formation of calcium carbonate); temperature change; and other chemical, physical, and biological reactions. The electrometric method of pH measurement described below applies to filtered or unfiltered surface water and ground water, from fresh to saline.

The pH of a water sample must be measured immediately in the field; laboratory-measured pH should not be relied on in place of field-measured pH.

Field conditions, including rain, wind, cold, dust, and direct sunlight can cause measurement problems. To the extent possible, shield the instrument and measurement process from the effects of harsh weather.

- ▶ In dry, windy climates, a static charge can build up on the face of a pH meter and cause erratic readings on the display.
- ▶ Polish the face of the display with a soft, absorbent tissue treated with several drops of antistatic solution (such as plastic polish) to minimize this interference.

TECHNICAL NOTE: Temperature has two effects on pH measurement of a sample: it can affect electrode potential (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect). The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample can be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

SURFACE WATER 6.4.3.A

It is generally preferable to measure pH in situ rather than on a sample taken from a splitter or compositing device. If stream conditions are such that water would pass the in situ pH sensor at a very high rate of flow, however, streaming-potential effects could affect the accuracy of the measurement. For such conditions, it is preferable to withdraw a discrete sample directly from the stream or compositing device and use the subsample measurement procedures described below. The pH instrument system should be set up on board the boat so that pH is measured at the time of sample collection.

Standard pH measurement in flowing surface water represents the cross-sectional mean hydrogen ion activity or median pH at the time of observation.

To compute a mean pH for the stream: (1) Sum the products of each subsection area, using the logarithm of the median pH determined for each subsection; (2) divide the sum by the total area of the cross section; and (3) convert back to pH by taking the antilogarithm of the quotient.

In situ measurement

Follow the 7 steps listed below for in situ pH measurement:

1. Calibrate a pH system on site (after equilibrating the buffers with the stream temperature, if necessary). Check the electrode performance (see "Electrode Maintenance," in 6.4.1) and the calibration date of the thermometer being used.
2. Record the pH variation from a cross-sectional profile, if possible, to determine if pH is uniform at any given discharge, and select the sampling method (NFM 6.0.2) appropriate for study objectives.
 - **Flowing, shallow stream**—Wade to the location(s) where pH is to be measured.
 - **Stream too deep to wade**—Lower a weighted pH sensor with a calibrated temperature sensor from a bridge, cableway, or boat. Do not attach the weight to sensor or sensor cables.
 - **Still-water conditions**—Measure pH at multiple depths at several points in the cross section.

3. Immerse the pH electrode and temperature sensor in the water to the correct depth and hold them there for at least 60 seconds to equilibrate them to water temperature.
4. Measure the temperature.
 - If the pH instrument system contains an automatic temperature compensator (ATC), use the ATC to measure water temperature.
 - If the instrument system does not contain an ATC, use a separate calibrated thermometer, adjust the meter to the sample temperature (if necessary), and remove the thermometer.
5. Record the pH and temperature values without removing the sensor from the water.
 - Values generally stabilize quickly within ± 0.05 to 0.1 standard pH unit, depending on the instrument system.
 - Record the median of the observed values.
 - If readings do not stabilize after extending the measurement period, note this difficulty on the field forms along with the pH readings, and record the median value of the last five or more readings.
6. EWI or EDI measurements—Proceed to the next station in the cross section. Repeat steps 3 through 5. After all stations in the cross section have been measured, rinse the sensors with deionized water and store them.
7. Record the stream pH on the field forms:
 - **In still water—median** of three or more sequential values.
 - **EDI—mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
 - **EWI—mean or median** of all subsections measured. (Note that pH values must be converted to a logarithm before calculating a mean value.)

Subsample measurement

When streams are fast-flowing or the water contains much sediment or algae, pH measurement of a discretely collected subsample might be preferable to in situ measurement. Representative samples are to be collected and split or composited according to approved USGS methods (Wells and others, 1990). pH measurement in fast-flowing streams should be made at the time of collection from a boat that has been set up for such measurements.

- ▶ Measure pH as soon as possible after compositing the EDI or EWI sample.
- ▶ Filter the sample if the pH continues to drift: measure pH in the field on both unfiltered and filtered subsamples and record both values on the field form.
- ▶ If the filtered sample provides the only stable pH value, report this value as sample pH.

TECHNICAL NOTE: Reported pH values are normally determined on an unfiltered sample. However, large concentrations of suspended sediment or algae can be a source of measurement error; slow settling of clay particles or algal respiration can cause “drift” of an observed pH value.

Throughout collection and processing, avoid excess aeration to prevent losses and gains of dissolved gases (especially CO₂) from solution.

1. Calibrate the pH system on site (after equilibrating buffer temperature with stream temperature, if necessary). Check the electrode performance (see 6.4.1).
2. Select the appropriate sampling method (see NFM 6.0) and collect a representative sample.
3. Withdraw properly homogenized sample(s) from the compositing device.
 - Rinse the collection bottles three times with the sample (use filtrate, if a filtered sample is used).
 - If the samples need to be stored for a short time or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient stream temperature, and measure pH in the field as soon as possible.
4. Rinse thoroughly with deionized water—the pH electrode, thermometer or ATC sensor, stir bar, and a measurement container.
 - For pH, follow the deionized water rinse of equipment with a rinse using sample water.
 - For ANC or alkalinity, rinse with deionized water only; do not rinse with the sample when using this equipment (see NFM 6.6).

5. Immerse electrode and temperature sensor in sample water for at least 60 seconds to equilibrate to sample temperature.
6. Pour fresh aliquot of the sample water into a container holding the electrode and thermometer. **Do not let the electrode touch the bottom or sides of container during measurement.**
7. Measure and record the initial temperature. Use the ATC, if it is available and calibrated, or use a separate calibrated thermometer and adjust the meter manually to the sample temperature (if necessary).
8. Establish equilibrium between the electrode(s) and sample by stirring **slowly** (no vortex) or by manual swirling.
 - Do not stir if a vortex is formed that affects the electrode performance.
 - Do not use a magnetic stirrer for samples with low conductivity (less than 100 $\mu\text{S}/\text{cm}$).
 - Before recording a pH value, allow the sample to reach quiescence.
9. Record the pH and temperature measurements on the field forms, along with the sampling, processing, and measurement methods used and any observed anomalies.
10. **Quality control**—Repeat steps 6 through 9 with at least two fresh subsamples to check measurement precision. Subsample values should agree within ± 0.1 pH unit (or study-determined criterion). Report the median of the values measured.
11. Rinse the electrode and temperature sensor thoroughly with deionized water. Replace the plug on the fill hole of refillable electrodes and follow the recommended storage procedure.
12. Discard the used sample into a waste container and dispose of it according to regulations.

6.4.3.B GROUND WATER

Measurements reported as ground-water pH must represent aquifer conditions (consult NFM 6.0 for guidance). Measure pH as close to the source as possible, either downhole or within a flowthrough chamber.

- Use equipment that minimizes aeration and operate equipment in a manner to help mitigate losses and gains of dissolved gases in solution (for example, carbon dioxide).

- ▶ Although downhole measurements are likely to be most representative of ground-water pH, proper use of pH instruments with flowthrough chambers can yield comparable values.
- ▶ The downhole system is not practical if samples will be collected after field measurements, because the instrument should not be left in the well during sampling and the pump should not be turned off between purging and sample collection—use a flowthrough-chamber system.
- ▶ Streaming potentials in the flowthrough chamber can result in biased pH values. Make the final (the reported sample pH) measurement in quiescent water.

Bailed or other methods for collecting discrete samples isolated from their source are not recommended for the determination of pH, although such methods are sometimes used owing to site characteristics or study requirements. Record the method used to obtain the sample for pH measurements on the field forms and in the data base.

Downhole and flowthrough-chamber measurements

1. Calibrate the pH instrument system on site.
 - a. If necessary, bring the buffer solutions to the temperature of the water to be measured (discharge the well water into a bucket while suspending the standards in a net bag; allow at least 15 minutes for temperature equilibration; check temperature of the water flowing into the bucket against that of the buffers).
 - Check that the thermometer has been District certified within at least the past 4 months.
 - Check electrode performance (see 6.4.1 and 6.4.2).
 - b. After calibration, rinse the pH electrode thoroughly with deionized water and blot it to remove excess water. Do not wipe the electrode.
2. Install the pH monitoring system for sample measurement (see 6.0.3 in NFM 6.0).
 - **Downhole system**—Lower sensors to the measuring point, followed by the pump, to monitor pH variation during purging.

- **Flowthrough system**—Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged. Check for and eliminate a backpressure condition.
3. During purging (see table 6.0–1 and fig. 6.0–3 in NFM 6.0):
 - Keep the flow constant and laminar.
 - Allow the sensors to equilibrate with the ground water for 5 minutes or more at the flow rate to be used for collecting all of the other samples.
 4. Record pH values at regularly spaced time intervals throughout purging. Compare the variability of the pH values toward the end of purging with the stability criterion:
 - The stability criterion is met when five readings made at regularly spaced intervals of 3 to 5 minutes or more are within 0.1 standard pH unit or less (depending on the equipment). Routine measurement must fall within the ± 0.1 unit criterion. When readings fluctuate rapidly, select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.
 - If the criterion is not met, extend the purge period in accordance with study objectives, and continue to record measurements at regularly spaced time intervals. Record any difficulty on the field forms.
 5. Measure and report the pH:
 - If using a flowthrough system, divert the flow from passing into the flowthrough chamber after recording the other field measurements. Measure the sample pH in the chamber as soon as the water is still. Take several readings to be sure that the system has stabilized.
 - If using a downhole method, measure the sample pH after pumping has ceased. This entails installing the downhole sensors in the well after sample collection. If field measurements only are being monitored, stop the pump (after recording the other field-measurement values) and allow the pH to stabilize before recording the pH value.
 - Report the final value measured on a quiescent (no-flow) sample, if the values are stable. If the stability criterion is not met, record the range of values observed for the time interval monitored, and report the median of the final five or more values observed.

Subsample measurement

pH measurements reported from bailed or other discrete samples need to be identified in the data base by a description of the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

Do not use a subsample method
if waters are reducing.

1. Calibrate the pH system on site (after equilibrating the buffers with the ground-water temperature, if necessary). Check the electrode performance (see sections 6.4.1 and 6.4.2).
2. Draw off a subsample through a bottom-emptying device that fits tightly over the bottle opening.
 - **Quality control**—Collect three subsamples to check precision.
 - Rinse the sample bottles three times with sample; use filtrate if filtered sample is used. Cap the bottles until they are ready for use.
 - If the samples need to be stored for a short time or if several subsamples will be measured, collect the sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient ground-water temperature, and measure the pH as soon as possible.
3. Follow the procedures described in steps 4 through 12 for subsample measurement of surface water (6.4.3.A).

TECHNICAL NOTE: An alternative method is to pour the sample into an open container instead of measuring it in a closed system. If this method is used and readings do not stabilize within several minutes, the cause may be out-gassing of carbon dioxide—measure the sample in a closed system. Filter the sample if settling of charged clay particles interferes with the stability of readings.